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# Atmosphere contamination following repainting of a human hyperbaric chamber complex

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Lillo RS. Morris JW, Caldwell JM, Balk DM, Flynn ET. Atmosphere contamination following repainting of a human hyperbaric chamber complex. Undersea Biomed Res 1990: 17(5):437-449.—The Naval Medical Research Institute currently conducts hyperbaric research in a Man-Rated Chamber Complex (MRCC) originally installed in 1977. Significant engineering alterations to the MRCC and rusting of some of its interior sections necessitated repainting, which was completed in 1988. Great care was taken in selecting an appropriate paint (polyamide epoxy) and in ensuring correct application and curing procedures. Only very low levels of hydrocarbons were found in the MRCC atmosphere before initial pressurization after painting and curing. After pressurization, however, significant chemical contamination was found. The primary contaminants were aromatic hydrocarbons: xylenes (which were a major component of both the primer and topcoat paint) and ethyl benzene. The role that pressure played in stimulating off-gassing from the paint is not clear; the off-gassing rate was observed to be similar over a large range in chamber pressures from 1.6 to 31.0 atm abs. Scrubbing the chamber atmosphere with the chemical absorbent Purafil was effective in removing the contaminants. Contamination has been observed to slowly decline with chamber use and is expected to continue to improve with time. However, this contamination experience emphasizes the need for a high precision gas analysis program at any diving facility to ensure the safety of the breathing gas and chamber atmosphere.

> diving off-gassing saturation diving

Atmospheric contamination can be a serious problem for closed environmental systems such as submarines, spacecraft, and saturation diving systems (1-3). Unfortunately, little information exists regarding control of atmospheric contaminants at hyperbaric facilities where diving operations may expose humans to high-pressure, closed atmospheres for extended periods. The few reports that have been published generally deal with specific incidents where exogenous chemicals have been introduced acutely into the system (4, 5).

In 1986, we reported (6) the occurrence of organic chemical contamination in the large Man-Rated Chamber Complex (MRCC) at the Naval Medical Research Institute (NMRI). This problem was believed due to faulty painting of the interior of the MRCC. After a significant decontamination effort and subsequent chamber use, the contamination eventually diminished to acceptable levels. However, significant engineering alterations to the MRCC and rusting of some sections of its interior necessitated repainting, which was completed in 1988. Because of the prior contamination problem, great care was taken in selecting an appropriate paint and in ensuring correct application and curing procedures during the repainting. This report describes the painting operation and the subsequent contamination problem that developed in the MRCC.

#### **METHODS**

# MRCC configuration and specifications

The MRCC consists of five chambers ("O", "R", "D", "I", "A") connected together in a row (Fig. 1). The center chamber, "D", consists of two sections, an upper part that remains dry, and a lower part that can be filled with water (wet pot). Interchamber hatches allow isolation of any chamber from adjacent chambers. Two chambers ("I", "A") have pressure ratings of 103 atmospheres absolute (atm abs); the other three ("O", "R", "D") have ratings of 69 atm abs. Each chamber has its own atmosphere conditioning system (ACS) which is designed to control CO<sub>2</sub>, O<sub>2</sub>, and temperature of the atmosphere. Each ACS loop consists of a plumbing circuit containing a gas circulating fan, moisture condenser, CO<sub>2</sub> scrubbing canisters, O<sub>2</sub> addition system, and heat exchanger. For exact dimensional specifications on the MRCC, see appendix A.

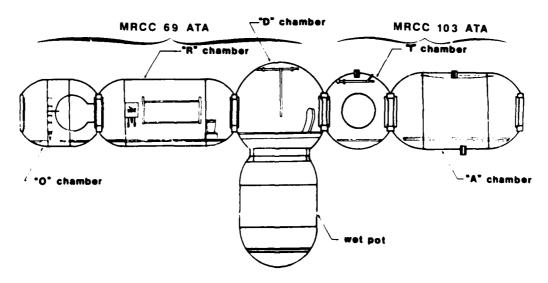


Fig. 1. MRCC configuration consists of five chambers connected together in a row. "D" consists of an upper part that remains dry, and a lower part (wet pot) that can be filled with water. For dimensional specifications, see appendix A.

# Selection of paint

Paint that is used on the interior of manned hyperbaric chambers should meet the following requirements: a) adequate flexibility so the paint deflects with the shell of the chamber; b) high resistance to water, abrasion, and alkali or acid solutions; c) fire resistance; and d) favorable off-gassing properties so that there is minimal release of solvents from the paint coating after final curing.

Past problems (observed during the early 1980s) resulting from the initial application of paint to the MRCC included severe blistering and peeling accompanied by offgassing of hydrocarbon solvents. These problems apparently were at least partly due to the use of a phenolic paint that did not flex with the chamber shell, and possibly to inadequate application procedures. Because of these earlier problems, NMRI took great care in the selection of an appropriate paint and in correct application and curing procedures.

Westinghouse Electric Corporation's Oceanic Division (Annapolis, MD) was awarded a contract to define the type of paint and the application procedures to be used. A polyamide epoxy coating system (Madewell 200; Madewell Products Corp., Roswell, GA) was selected for the MRCC based on the Technical Survey (7) and the Engineering Document (8) from Westinghouse, as well as on the prior experience of other hyperbaric facilities (e.g., the Defence and Civil Institute of Environmental Medicine, Toronto, Canada). This two-component system was expected to exhibit good resistance to immersion, chemicals, and fire and to present no off-gassing or toxicity problems. For more information on the Madewell 200 paint system and its reported hazardous ingredients, see appendix B.

# Chamber painting

The MRCC was painted in two separate operations. First, "D", "R", and "O" chambers were prepared, painted, and cured from 27 September to 23 October 1987; next, "A" and "I" were treated in similar fashion from 3 to 18 February 1988. Application procedures were based on the Engineering Document from Westinghouse (8) and recommendations from the manufacturer.

Before surface preparation, all loose equipment, furnishings, and hardware were removed from the interior of the MRCC. The stripped interior steel shell was then prepared for painting by first cleaning the surface with Tek-317 (Bio-Tek Industries. Inc.; a concentrated form of Formula 409 or Fantastic) to remove oil and grease. All viewports and penetrators were then covered for protection, and the interior was grit-blasted to remove the old Phenoline paint, existing rust, and to smooth any pitting of the surfaces. An initial primer coat was applied to all surfaces, followed by two ioncoat applications to all chambers. A third topcoat application was applied to the wet pot and wetted sump areas (under the deck plates) of all chambers. Between application of each coat of paint, the chambers were closed and purged with hot (46°C), dry (0–10% relative humidity) air. This was done to facilitate curing by removal of paint solvents from the paint coating. Such procedures would discourage entrapment of these solvents in the intermediate paint layers. The hot air purge was conducted for 12 h between each coat. Upon completion of the final coat of paint, the chambers were once again closed and purged with hot, dry air. For the final purge, the air temperature was set at 60°C and the purge was conducted for 5 days.

The increase in air temperature was intended to maximize the off-gassing (i.e., by raising the vapor pressure) of the paint solvents. The only limitation of the temperature was the temperature rating of the insulation on the exterior of the chambers. The final coverage of paint had an average dry film thickness of 7 mils in areas where three coats were used and 10 mils for four coats.

# Pressure certification

After a major overhaul and refit, the MRCC systems underwent testing for recertification. Recertification tests were conducted in accordance with U.S. Navy Diving and Manned Hyperbaric Systems Safety Certification Manual (9). This testing required the chamber complex to be pressurized to full working pressure and all subsystems to be operated at that depth. Upon successful completion, the Naval Facilities Engineering Command System Certification Authority (NAVFAC SCA) approved recertification for 5-yr. Recertification by the NAVFAC SCA was granted for the 1000-psig chambers in February 1988 and for the 1500-psig chambers in November 1988.

# Testing for contamination

Testing for atmospheric contamination involved closing the hatches of specific chambers and letting the closed chambers sit for a time at either 1 atm abs or at pressure. This "soaking time" allowed any chemicals off-gassing from the chamber interior to accumulate. Air or He, normally used for diving operations and previously checked for purity, was used for pressurization. In some cases, initial samples of gas were taken immediately at the start of the soak after pressurization to confirm purity. Except during manned dives, no gas was added during the test after initial pressurization to avoid dilution of the chemicals. Because of small chamber leaks, pressures at the end of unmanned tests were usually slightly below the starting pressures. Chambers were tested either together (i.e., with hatches open between them) or separately (i.e., with hatches closed between the chambers). For pressurized tests of separated chambers, a pressure differential was maintained between adjacent chambers to facilitate keeping the interchamber hatch sealed. The wet pot was filled with water during some tests and left dry during others.

Chamber gas was circulated using the ACS loops for approximately 1 h before sampling to thoroughly mix the atmosphere. In addition, such mixing was generally performed for short periods during the test, depending on operational considerations. Scrubbing canisters (for CO<sub>2</sub> removal) in the ACS were kept empty during most of these tests, although a combination of Sodasorb (a mixture of NaOH and CaO; W.R. Grace & Co., Atlanta, GA) and Purafil [alumina with potassium permanganate as an oxidizing agent; Purafil Inc., Atlanta, GA (10)] was placed into the canisters to absorb gas contaminants during several tests as well as during manned diving operations. In all but one unmanned test (as noted), the chambers were tested after all easily removable gear and equipment (i.e., hoses, masks, bunks) were taken out. This prevented these items from contributing to the off-gassing load and confounding the interpretation of the results. Thus, under these conditions, only the chambers themselves were being tested. Although we also routinely test for the safety of gear that will go inside the MRCC, these data will not be reported here. During manned

dives, men and equipment are inside the diving complex and are important variables in the test results. As already mentioned, gas composition is also continuously being controlled during diving operations by removal of  $CO_2$  and addition of  $O_2$  via the ACS.

A summary of the gas sampling tests that will be discussed in this report with specific test conditions is in Table 1. Unfortunately, in certain instances testing was scheduled around and limited by chamber maintenance and diving operations. Thus, experimental designs herein were often dictated largely by MRCC schedules.

# Sampling and analysis

Gas sampling procedures will be briefly described here, although the sampling methodology used at NMRI has been previously reported in detail (11). Gas samples were obtained from the MRCC using 500-ml stainless steel cylinders that had been heated and evacuated to 30-60 millitorr and were generally collected in duplicate (two cylinders/sample site). When sampling was done from pressurized chambers, cylinders were filled by either one or two methods. For the majority of tests not involving human subjects, cylinders were filled via a clean, stainless steel whip connected to chamber plumbing after allowing gas flow to purge all hardware for 3-5 min. Sample pressure was reduced by a regulator if chamber pressure exceeded approximately 8 atm abs. MRCC hardware that the gas contacted during sampling included metal tubing, one or more high pressure valves, and one high purity regulator (if used). All hardware had been previously cleaned to O<sub>2</sub>-safe specifications (12). During diving operations when men were inside the chamber, cylinders were "locked" into the pressurized chamber. A diver could then open the cylinder to the inside atmosphere, close it, and lock it out. This procedure avoided the potential problems associated with flowing a sample through the tubing, regulator, and valves during which the composition of the gas could change.

Samples from unpressurized (1 atm abs) chambers were obtained by one of two methods. The first involved opening an evacuated cylinder inside the chamber immediately upon opening the chamber door (test A.1). Subsequently, the cylinder was backfilled to approximately 3.0 atm abs with hydrocarbon-free gas, and several hours allowed for cylinder contents to equilibrate before analysis. The second procedure involved cylinder pressurization to approximately 3.7 atm abs using a stainless steel bellows pump (model MB-151, Metal Bellows Corp., Sharon, MA) placed inside the chamber, again immediately after opening the chamber door (test A.2).

In addition to collection of gas samples for later analysis, the chamber gas was often analyzed as it flowed out of the MRCC, using a portable Photoionization Detector (PID, model PI 101; HNU Systems Inc., Newton Highlands, MA). These measurements were taken at the same locations on the outside of the complex where gas samples were normally obtained. For PID readings, a 5-ml plastic syringe barrel was attached to a metal luer connector at the point where gas exited the metal piping of the MRCC. Before use, the PID was calibrated using a gravimetric standard of isobutylene/balance air at a concentration of approximately 12 ppm certified to  $\pm 2\%$  relative of stated value (Scott Specialty Gases, Plumsteadville, PA). The PID, which is a general hydrocarbon analyzer, was equipped with a 10.2 ev UV lamp. This lamp gave it sufficient sensitivity to detect <1 ppm of aromatic hydrocarbons, such as toluene and xylenes, which are common constituents of many paints. Although the

TABLE 1
RESULTS OF GAS ANALYSIS BY GAS CHROMATOGRAPHY<sup>4</sup>

Test	Date	Chambers	Pressure, atm abs	Soak Time, h	Xylenes	Ethyl Benzene	Others
Painti	ng of D. I	R, O 9/27/87-	-10/23/87	<del></del>			
Al	10/87	D,R,O	1.0	60	0.2	_	
Painti	ng of A, I	2/3/88-2/18/	/88				
A2	2/88	A,I	1.0	62.5	0.7		
В	2/88	D,R,O	3.4/4.0/3.4		D 11.0R	1.0	SB
					<b>37.40</b>	4.5	SB
				91	6.9	0.8	SB
D	3/88	D,R,O	7.0/7.6/7.0	25.5			
E1	3/88	D,R,O	1.6/1.9/1.6		D NM	NM	
					R 7.1	0.6	SB
				71	O 7.4	0.8	SB
E2	3-4/88	D,R,O	7.0	6	0.8	_	
				24	2.0		
				48	5.2	-	
E3	4/88	D,R,O	31.0	22	3.2	<del></del>	
				46	4.0	<del></del>	
	4 (0.0	5.50		71	6.8		
E4	4/88	D,R,O	1.6/1.9/1.6	24	D 4.4		
					R 4.1 O 0.4		
-	4100		1 4/1 0	•			
F	4/88	A,I	1.6/1.9	24	A 1.1	-	
_	<b>7</b> (00	5.50	. =	2.51	I 2.5		
G	7/88	D,R,O	1.7	2–71		_	
HI	1/89	Α	4.0	1			
				90	1.9	<del>-</del>	
112	1/00	D D O I	4.0/4.6	,	D 2 6	-	
H2	1/89	D,R,O,I	4.0/4.6 4.0/4.0	1 57	D 3.6 R 5.0	0.4 0.4	
			4.0/4.0	31	O 1.1	0.4	
					I 3.7	0.4	
Н3	2/89	A,D	4.0	I			
113	<b>2</b> , 0 7	1 1 1 1 2	***	61.5	A 0.4	1.2 Toluene	
					D 0.9		
1	2-5/89	MRCC	5.5	1-12	~_	_	
•		MINCC	5.5	days	_		

<sup>&</sup>quot;Values in ppm SEV (excluding methane): dash indicates < 0.1 ppm uncorrected for depth; xylenes include ortho, meta, and para isomers: l = initial sample immediately after reaching depth at start of soak test; one test pressure indicates chambers tested together, multiple pressures indicate chambers tested separately; SB = aliphatic-substituted benzenes, < 1 ppm SEV; NM = samples not meaningful because chamber leaked excessively during test. Continued on next page.

#### Tests:

- A. First tests of MRCC after painting but before initial pressurization of any chamber. Tests began on the same day that final paint curing was completed.
- B. First test of "D", "R", and "O" after exposure of chambers to pressure of 31.0 atm abs.
- C. Test of "D", "R", and "O" performed to monitor hydrocarbons using a Photoionization Detector (results in Fig. 2).
- D. Scrubbing test with "D", "R", and "O" using the ACS of each chamber to circulate continuously the chamber gas through canisters filled with Purafil or a 50:50 mixture of Purafil and Sodasorb.
- E. Test series with "D", "R", and "O" to evaluate contamination problem.
- F. First test of "A" and "I" after exposure of chambers to pressure of 4.0 atm abs.
- G. Multiple samples from MRCC during 3 air saturation, manned dives.
- H. Test of MRCC before beginning of second manned saturation dive series. All gear, including research equipment, to be used for the upcoming saturation dive was inside during test H3.
- Multiple samples from MRCC during 3 manned saturation dives with HE-O<sub>2</sub>. Test A. First test
  of MRCC after painting but before pressure exposure.

PID is a fairly nonselective instrument that responds to a broad range of hydrocarbons, it can be used as an effective screening tool. In instances where the chemical contaminants have been identified, quantitation may be possible if the sensitivities of the chemical species relative to the calibration gas (i.e., isobutylene) are known.

Gas samples from stainless steel cylinders were analyzed by gas chromatography (GC) using a Shimadzu GC-9A temperature-programmable gas chromatograph (Shimadzu Corp., Columbia, MD) interfaced with two different detection systems. Most samples were analyzed with a flame ionization detector (FID) linked to a methyl silicone-packed column (SP-2100, Supelco Inc., Bellefonte, PA), which was ramped from 50° to 150°C. Gas samples (0.5 ml) were introduced into the FID via a gas sampling valve. For samples collected at great depth (i.e., 1000 fsw), there was the unavoidable problem of dilution of off-gassing chemicals due to the increased amount of gas in the chamber at greater pressures. This necessitated greater detection sensitivity than that normally achieved with direct gas injection into the GC. For these samples, contaminants in the gas were preconcentrated on Tenax before introduction into the GC, using a Tekmar sample concentrator (model LSC-2, Tekmar Co., Cincinnati, OH). Subsequent thermal desorption of the Tenax allowed introduction of a concentrated bolus of contaminants into the GC. This system used a Supelcowax 10 wide-bore (0.75 mm) glass capillary column (Supelco, Inc.) interfaced with a H-P model 5970B mass spectrometer (MS: Hewlett-Packard Co., Palo Alto, CA). For this application, the GC oven was ramped from 40° to 150°C. A FID would have been satisfactory in most cases (i.e., quantification of known contaminants) for use with the concentrator rather than the more complicated MS. However, the Tekmar-GC-MS system was already configured and operational, so it was used. For identification of the few unknown chemicals that were detected, the MS was absolutely necessary.

Instruments were calibrated using gravimetric standards containing a mixture of approximately 2 or 10 ppm each of Freon 113; 1.1.1 trichloroethane; benzene; toluene; and o-.m-,p-xylenes certified to  $\pm 1$ -2% relative of stated value (Scott Specialty Gases). Precision associated with trace hydrocarbon analysis using the FID ranged from 1 to 5% relative, depending on the particular chemical. Precision for the Tekmar-GC-MS system was <20% relative for all chemicals. Detectability of most hydrocarbons with GC using a FID is at least 0.1 ppm or less with fairly standard procedures; with the Tekmar-GC-MS, detectability can be considerably lower than 0.1 ppm (i.e.,

ppb or ppt). Results from analysis are reported in surface equivalent values (SEV) after correction for the pressure of the chamber at which the sample was obtained.

Example: 2 ppm toluene measured at 1 atm abs using GC in gas from a chamber tested at 4 atm abs would have a SEV equal to 8 ppm  $(2 \text{ ppm/1 atm abs} \times 4 \text{ atm abs} = 8 \text{ ppm})$ .

# **RESULTS**

Analytical results from the gas sampling tests are in Table 1, which lists the levels of xylenes and ethyl benzene because these were the most common contaminants found. In addition, other chemicals that were estimated as >0.1 ppm are indicated.

#### Test A

After painting and curing of "D", "R", and "O", preliminary testing revealed minimal organic contamination (<1 ppm hydrocarbons excluding methane) after soaking at 1 atm abs for 60 h. Similar results were obtained from "A" and "I" several months later.

#### Test B

After pressure certification at 31.0 atm abs, significant chemical contamination (15-50 ppm SEV total hydrocarbons excluding methane) was unexpectedly observed in "D", "R", and "O" after a 91-h soak at 3.4-4.0 atm abs. Primary contaminants were the aromatic hydrocarbons, xylenes (which were a major component of both the primer and topcoat paint and by far the most predominant contaminant), and ethyl benzene. A number of other compounds were found in amounts <1 ppm SEV. By using mass spectroscopy, most of these latter compounds were identified to be other aliphatic-substituted benzenes, which are common constituents of commercial aromatic solvents.

# Tests C and D

Monitoring the chamber atmosphere of "D", "R", and "O" with a PID for approximately 1 day showed that hydrocarbon levels increased with time (test C, Fig. 2). After the chemical absorbent Purafil was loaded into the canister of the ACS loop of "D", hydrocarbon levels began to decline. After this, another test (D) showed that hydrocarbons could be maintained at low levels for 1 day by scrubbing the atmosphere with the ACS canisters filled with Purafil. This was confirmed both by analysis of the end-dive sample as well as by periodic PID readings during the test.

# Test E

This test series evaluated the contamination problem. Results (Table 1 and Fig. 3) indicated that hydrocarbons accumulate in the chambers with time but, interestingly, the off-gassing rate does not seem to be affected by a 20-fold range in testing pressure. Contamination levels after this test series seemed similar to that observed before.

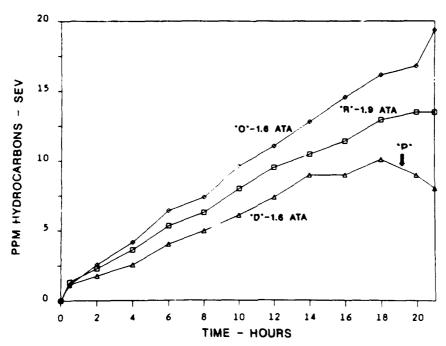


Fig. 2. Test C. Hydrocarbon levels increase with time in "D", "R", and "O" when chambers are left pressurized at 1.6 or 1.9 atm abs with all ACS loop canisters empty. At time indicated by "P", Purafil was loaded into the canister of the ACS loop of "D". A decline in the hydrocarbon level of "D" was then observed as gas was circulated by the ACS. Measurements were made with a PID.

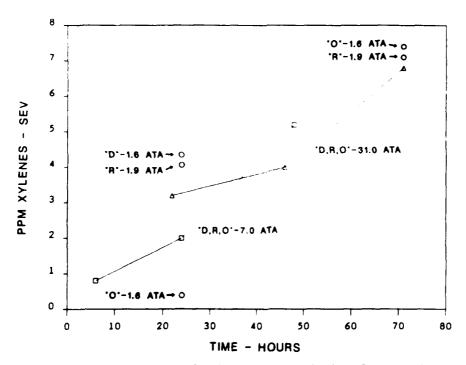


Fig. 3. Hydrocarbon levels (in terms of total xylenes) increase in "D", "R", and "O" when chambers are left pressurized at depths ranging from 1.6 to 31.0 atm abs. Testing pressure does not seem to affect the rate of hydrocarbon buildup. Data taken from test series E (Table 1).

The reason for the relatively low reading of 0.4 ppm for "O" during test E.4 is not known.

#### Test F

As was the case with "D", "R", and "O" significant chemical contamination (several parts per million hydrocarbons after a 24-h soak at 1.6-1.9 atm abs) was observed in "A" and "I" after these chambers had been exposed to pressure. Again, the contamination was primarily xylenes.

# Tests G and I

These tests include numerous samples taken during 3 manned saturation dives at 1.7 atm abs and 3 manned dives at 5.5 atm abs. Samples were drawn after dive times of up to 12 days. Negligible contamination was observed during diving operations with the ACS loops operating and gear and men inside. Presumably the scrubbing action of the ACS loops removed the chemicals as they off-gassed into the interior of the MRCC.

# Test H

Significant aromatic hydrocarbon contamination still existed in the MRCC 1 yr after repainting and after numerous diving operations. Interestingly, when two chambers were retested with equipment inside (test H.3), xylene levels were lower, and approximately 1 ppm of toluene was detected. The "softgoods" inside the MRCC undoubtedly absorbed some of the off-gassing from the paint. Small amounts of toluene have been seen before and during off-gassing tests on some of the research equipment that had been fabricated inhouse using adhesives, and such items probably account for the toluene in this case.

#### DISCUSSION

This and past reports (5, 6, 13) suggest that the paint used for the interior of diving systems can be a significant source of chemical contamination. Although the inside of a hyperbaric chamber is normally painted to prevent rusting, we are unaware of any nontoxic paints that are appropriate for use with manned diving systems. Most paints except for water-based types, contain large amounts of organic solvents, including hazardous aromatic hydrocarbons (i.e., toluene, xylenes, and other aliphatic-substituted benzenes). Such paints have the potential for harmful off-gassing after application. Unfortunately, present findings indicate that strict adherence to paint application and curing procedures, as suggested by the manufacturer, does not ensure a safe environment after painting.

This report has shown that only low hydrocarbon levels (<1 ppm) were detected soon after painting and curing procedures had been completed. However, the situation changed markedly after initial exposure of the chambers to pressure, when a much higher contamination was observed. The development of a significant paint offgassing problem after pressure exposure was not totally unexpected, although the

magnitude of the contamination was surprising. A similar experience at NUTEC (13) was described where diving chambers that had been recently painted gave off no noticeable odor before compression. At pressure (21 or 46 bar heliox), significant amounts (approximately 10-20 ppm) of hydrocarbons, attributed to the paint and/or primer, were detected.

Estimation of potential health hazards associated with chemical contamination is always difficult. For hyperbaric exposures, the problem is more complex due to the paucity of information on contaminant effects on humans (or animals) at pressure. Unfortunately, existing guidelines for dealing with chemical hazards in a variety of environments (1, 3, 9, 14-19) are inadequate to evaluate the safety of diving atmospheres and gases. However, such recommendations on chemical exposure can provide some guidance, particularly with certain compounds. In the present contamination situation with the MRCC, the predominant contaminant was xylene. Following initial pressurization after painting, xylene levels approached 50% of the 8-h timeweighted average (TWA) limit of 100 ppm set both by the National Institute for Occupational Safety and Health (17) and by the American Conference of Governmental Industrial Hygienists (16), and 100% of the National Research Council's (18) 90day limit of 50 ppm. Small amounts of ethyl benzene (1-2 orders of magnitude lower than its TWA value of 100 ppm) and other aliphatic-substituted benzenes (not positively identified) were also observed. These total aromatic levels greatly exceeded current 90-day exposure limits of 10 mg/m<sup>3</sup> for U.S. submarines (15), as well as current total hydrocarbon limits (less methane) of 10 ppm specified by the U.S. Navv for hyperbaric systems (9) and total hydrocarbons (less methane and Freon) of 10 ppm by the U.S. Navy Diving Manual (14). A substantial drop in contamination occurred in the next several months during chamber use, with xylene reaching levels well below its limits and only trace amounts of other chemical species detected. These results, especially the higher contaminant levels obser ed in the early samples, suggest that safety of manned diving operations could be assured only under condition of continuous scrubbing of the atmosphere with Purafil.

The role that pressure played in stimulating off-gassing from the paint is not clear. Penetration of helium or air into the paint coating under high pressure and the subsequent driving out of volatile compounds into atmosphere have been offered as one hypothesis in the NUTEC report (13). Similar ideas have been suggested by people in the diving community. However, under this scenario, increasing pressure should increase the rate at which the chemicals are driven out. This clearly was not the case in the MRCC, where the off-gassing rate did not seem affected by the test pressure. A more plausible answer is that the flexing and expansion of the chamber walls that occurred during compression after painting may have produced irreversible change to the paint surface that allowed any solvents trapped during curing to diffuse out at a faster rate. Whether this phenomenon involved cracking and tearing in the paint surface at the microscopic level is not known. No cracks in the MRCC paint surface were visible to the naked eye. Certainly the chamber surface is subjected to expansion, as evidenced by the increase in the water capacity of the wet pot by an additional 50 gallons at 31.0 atm abs compared to that at the surface. It would not be surprising if such expansion could crack the surface of the paint.

It is fortunate that hydrocarbon levels seem to remain at acceptable levels during diving operations. Presumably, off-gassing chemicals are being scrubbed out of the atmosphere by the absorbent Purafil during circulation through the ACS loops, as

was demonstrated during the chamber scrubbing tests. According to literature from Purafil, Inc. (10), contaminant molecules are first absorbed onto the microporous surfaces of the  $Al_2O_3$  substrate, then absorbed into solution with potassium permanganate, where oxidation to  $CO_2$  and  $H_2O$  occurs. The manufacturer apparently has conducted extensive testing on the effectiveness of Purafil for air purification. At NMRI, we have done no tests other than those reported. Thus, we cannot comment on how well Purafil works with various contaminants and under different conditions, particularly at high pressures.

Contamination inside the MRCC seems to be slowly declining with chamber use and is expected to continue to improve with time. However, this contamination experience at NMRI reemphasizes the need at all diving facilities for a high-precision gas analysis program to ensure the safety of the breathing gas and chamber atmosphere. Our experience performing gas analysis in support of diving operations during the past 5 yr has repeatedly reconfirmed this need. Hyperbaric facilities must have a capability to sample and analyze breathing gas accurately for trace contaminants if chemical incidents are to be handled intelligently and promptly.

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# **APPENDIX A**MRCC Dimensions

Chamber	Diameter, in.	Length, in.	Volume, ft <sup>3</sup>
0	84	96	259
R	84	172	504
D upper	108 (sphere)	_	602
lower (wet pot)	101	139 (height)	555
I	96 (sphere)	_	258
Α	96	183	656

# APPENDIX B Information on Madewell 200 Polyamide epoxy coating system<sup>a</sup>

- 1. Manufacturer: Madewell Products Corp., P.O. Box 902, Roswell, GA 30077, 404/475-8199.
- 2. Description:
  - a) 2-component polyamide epoxy coating system for use on properly prepared metal surfaces in immersion and nonimmersion services;
  - b) exhibits good chemical resistance and cures to a hard, abrasion-resistant finish;
  - c) primer has an inhibitive (nonlead) pigment added to help prevent corrosion in the event of physical damage to the topcoat.
- 3. Finish and Color:
  - a) 201 Primer—flat, grey;
  - b) 200 Topcoats—gloss, various colors available.
- 4. Hazardous Ingredients [taken from Material Safety Data Sheets furnished by Madewell Corp.]
  - a) Primer (2 parts): 201A primer grey, part A 201B primer converter, part B

	Percent by Weight			
Chemical	Part A	Part B	Part A + Part B	
Xylene		20	10	
Solvent naphtha (petroleum, light				
aromatic)	10	15	15	
Propylene glycol monomethyl ether	15	5	10	
Diacetone alcohol	5	_	5	

b) Topcoat (2 parts): 200A topcoat, part A

200B topcoat converter, part B

	Percent by Weight			
Chemical	Part A	Part B	Part A + Part B	
Xylene	15	5	20	
Solvent naphtha (petroleum, light aromatic)		10	5	
Propylene glycol monomethyl ether	5	15	10	
Diacetone alcohol	5		5	

Taken from Madewell Corp. literature; no. 7182-236, material safety data sheets on 200 series polyamide epoxy topcoat and primer)